

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

<p>16320A/09 A25 (A35) ICIL 12.09.74          IMPERIAL CHEM INDS LTD *GB 1502-777          12.09.74-GB-039815 (01.03.78) C08g-18/14 C08I-75/04          Forming polyurethane foam scrap into blocks - by coating with an aq. emulsion of polyisocyanate or prepolymer and compressing</p>	<p>A(5-G1E, 11-C3, 12-A5F, 12-S2), 156          cyanate with <math>\geq 1</math> monomeric polyols, e.g. ethylene glycol, trimethylol propane, etc.</p>
<p>Polyurethane foam scrap is reconstituted into a block of foam by coating the scrap with an aq. oil-in-water emulsion of a mixt. of methylene bridged polyphenyl polyisocyanates contg. di-, tri- and poly-isocyanates, or a prepolymer of such a mixt. The coated scrap is then held in contact under compression until cured into a solid mass. The scrap is pref. rigid foam, and the emulsion pref. contains a non-ionic surfactant devoid of OH, amino or CO<sub>2</sub>H gps.</p> <p><u>USE/ADVANTAGES</u>          The foam is of high density and is suitable for flooring, e.g. in freezers, and for thermal insulation.</p> <p><u>DETAIL</u>          The polyurethane can be made wholly or partially by polymerisation of polyisocyanates to yield isocyanurate foams, or from isocyanates plus OH-contg. cpds. The scrap is pref. in 1/16 inch-1 inch pieces. The prepolymer is made by reacting the mixt. of polyisocyanates with OH-ended polyethers or polyesters, or by reacting an excess of iso-</p>	<p>The surfactant is e.g. a condensate of alkyl phenols, long chain alcohols and amides with ethylene oxide, the end OH-gp. being etherified or esterified. Esp. pref. surfactants are of formula: RO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CONHX (where R is 1-4C alkyl; n is an integer such that the cpd. contains an average of <math>\geq 5</math> oxyethylene gps.; and X is the residue of a di- or poly-isocyanate, contg. <math>\geq 1</math> free isocyanate gp.). R is pref. CH<sub>3</sub>, and n is pref. 5-20. X can be derived from a mixt. of methylene bridged polyphenyl isocyanates or prepolymer thereof.</p> <p>The surfactant can be made in situ during prepn. of the emulsion. It is pref. derived from a cpd. RO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H of mol.wt. 300-600. The emulsions pref. comprise 10-90 pts wt. organic isocyanate of surfactant, there pref. being 10-66 wt.% of water. The coated scrap is compressed at 70-100°C for about 15 mins., to a compression of 2-5 times by vol. Pref. 10-70% isocyanate or prepolymer is used, based on wt. of foam scrap. The emulsion also opt. contains wood chip, scrap polystyrene, nucleating agents, flame retardants etc.</p> <p style="text-align: right;">GB1502777+</p>

## PATENT SPECIFICATION

(1) 1 502 777

1 502 777

- (21) Application No. 39815/74 (22) Filed 12 Sept. 1974  
(23) Complete Specification filed 24 July 1975  
(44) Complete Specification published 1 March 1978  
(51) INT CL<sup>2</sup> C08G 18/14  
(52) Index at acceptance C3R 32E6 32G1X 32G1Y 32KG 32PX  
(72) Inventors PETER MAYRHOFER and ALAN METCALFE  
WOOLER



## (54) POLYURETHANE FOAMS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the reconstitution of scrap polyurethane foam in the form of cuttings, chippings, powder and off-cuts into a reconstituted block of foam and is particularly applicable to rigid polyurethane foam scrap.

Polyurethane foam is made by reaction of polyisocyanates with polyhydroxy compounds and is manufactured in large blocks which are then cut and fabricated into any desired shape. During these fabrication operations various off-cuts and trimmings are produced which are too small in size and too irregular in shape to be used as such; additionally particulate foam is produced during cutting or sawing operations. This material which may be generically described as foam scrap is a liability to the manufacturer in that it is costly to produce, very few outlets are available for the scrap, and its disposal, particularly as quite large volumes are involved, presents an environmental problem.

The same problem arises in connection with isocyanurate foam made by the polymerisation of isocyanates optionally in the presence of small quantities of hydroxyl compound.

We have now found that this foam scrap may be reconstituted into blocks or moulded shapes of foam by the application of an aqueous emulsion of certain polyisocyanates as bonding agents to the scrap followed by compression of the scrap and bonding agent to the desired shape and size until the whole forms a reconstituted block of foam.

Thus according to the present invention there is provided a process for bonding together polyurethane foam (as hereinafter defined) scrap into a reconstituted block of foam which comprises coating the scrap with an aqueous oil in water emulsion of a mixture of methylene

bridged polyphenyl polyisocyanates containing diisocyanates, triisocyanates and higher functionality polyisocyanates or a prepolymer of such a mixture and holding the coated scrap in contact under compression until cured into a solid mass.

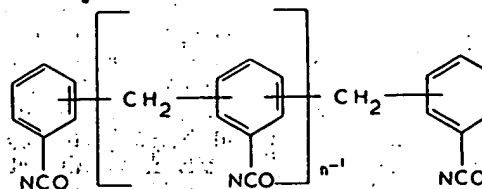
The process is particularly useful for the reconstitution of rigid foam scrap.

The term polyurethane foam used in the above description of the invention and later in the specification and claims embraces isocyanurate foams made wholly or partly by the polymerisation of isocyanates in addition to the normal polyurethane foams made by reaction of isocyanates and hydroxyl compounds.

The size of the scrap foam is not of great matter but obviously more homogeneous blocks of reconstituted foam will be obtained if the scrap material is in pieces of roughly the same size. The use of a mixture of scrap particles of graded sizes may assist in obtaining a more consolidated product which requires less compressing but may require the use of more emulsion. The pieces of scrap may conveniently range in size from 1/16" to 1".

As polyisocyanates for use in the present invention there may be used for example any mixture of methylene bridged polyphenyl polyisocyanates particularly crude mixtures of methylene bridged polyphenyl polyisocyanates containing diisocyanates, triisocyanates and higher functionality polyisocyanates which are available commercially under a variety of trade names.

Methylene bridged polyphenyl polyisocyanates are well known in the art and have the general formula



where n is one or more and in the case of the crude mixtures represents an average of more than one. They are prepared by phosgenation of corresponding mixture of polyamines obtained by condensation of aniline and formaldehyde.

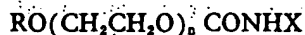
Isocyanate-ended prepolymers of mixtures of methylene bridged polyphenyl polyisocyanates may also be used in the present invention. Such prepolymers may be made by reacting the mixture of polyisocyanates with hydroxyl-ended polyethers or polyesters known for the manufacture of polyurethanes. Such prepolymers may be made using known techniques by reacting an excess of isocyanate with hydroxyl-ended polyether or polyester. There may also be used isocyanate-ended prepolymers obtained by reacting an excess of isocyanate with a monomeric polyol or mixture of monomeric polyols such as ethylene glycol, trimethylol propane or butane-diol. By an excess of isocyanate is meant an excess in the total isocyanate groups over the total hydroxyl groups present in the polyether or polyester used.

The isocyanates or prepolymers thereof used in the present invention in the form of aqueous oil in water emulsions, in particular oil in water emulsions incorporating non-ionic surface active agents devoid of hydroxy, amino or carboxylic acid groups.

Emulsions of isocyanates suitable for use in the present invention are described in UK Patent Specification No. 1444933.

Non-ionic surface active agents devoid of hydroxy, amino or carboxylic acid groups useful in the present emulsions may be any such agents in particular condensates containing chains of ethylene oxide molecules and no free chain end hydroxy, amino or carboxylic acid group. These include for example condensates of alkyl phenols, long chain alcohols and amides with ethylene oxide, the end hydroxy group being for example etherified or esterified.

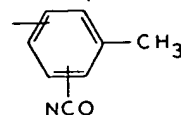
Of particular value are the reaction products of diisocyanates and higher functionality polyisocyanates with monoalkyl ethers of polyethylene glycols. These particular surface active agents or emulsifying agents have the formula



wherein R is an alkyl group of from 1 to 4 carbon atoms, n is an integer such that the compound contains an average of at least 5 oxyethylene groups and X is the residue of a di or polyisocyanate and contains at least one free isocyanate group. Examples of R include ethyl, propyl and butyl, preferably methyl. There must be sufficient oxyethylene groups  $(CH_2CH_2O)$  present in the surface active urethane that there is an average of at

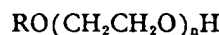
least 5 such groups per molecule. It is preferred that n represents an average of from 5 to 20.

The group X is the residue which would remain after one isocyanate group had been removed. The group X may be the residue of any diisocyanate or higher polyisocyanate and for example if the diisocyanate is a tolylene diisocyanate the residue X will be



Isocyanates from which the group X is derived include mixtures of methylene bridged polyphenyl polyisocyanates and isocyanate ended prepolymers thereof.

Such surface active urethanes may be manufactured by reacting an alcohol of the formula



with an isocyanate having at least two isocyanate groups, there being used at least one molar proportion of isocyanate group for each molar proportion of the alcohol. Preferably an excess of the isocyanate is used.

The reaction may be carried out by adding the alcohol to the isocyanate and allowing the reaction to proceed, preferably by heating the reaction mixture at a temperature of 50—150°C. Alternatively the reaction can be carried out at lower temperatures e.g. 25°C in the presence of a small amount of catalyst e.g. triethylene diamine.

In order to obtain emulsions for use in the present invention, the above type of surface active agent may be prepared in situ in the isocyanate. Thus if it is desired to produce an emulsion of a mixture of methylene bridged polyphenylpolyisocyanates, a small amount of the polyethyleneoxy alcohol



may be added to a large excess of the mixture of isocyanates and the emulsifying agent formed in situ in the isocyanate mixture.

In the cases where a prepolymer is to be used, formation of the polymer and an in situ surfactant may be carried out simultaneously or as two separate steps and the prepolymer/surfactant then mixed with water to give the emulsified prepolymer.

Thus when the prepolymer present in the emulsion is to be one of the class of preferred prepolymers mentioned hereinbefore, namely a prepolymer of a mixture of methylene bridged polyphenyl polyisocyanates containing diisocyanate, triisocyanate and higher functionality polyisocyanates (referred to hereinafter as MDI for convenience), the

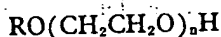
emulsion of the prepolymer may be made by any of the following three methods.

(1) Reaction of the MDI with the required amount of polyol to give the prepolymer followed by reaction with a small amount of the polyethyleneoxy alcohol



followed by emulsification by agitation with water.

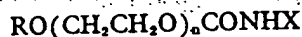
(2) Reaction of the MDI with the required small amount of the polyethyleneoxy alcohol



followed by reaction with the amount of polyol required to give the prepolymer followed by emulsification.

(3) Reaction of the MDI with the required amount of polyol and polyethyleneoxy alcohol simultaneously followed by emulsification in water.

In the above three methods the preparation of the surfactant is carried out in situ in the isocyanate, the surfactant being of the general formula



where X is the residue of the isocyanate and R is an alkyl group of from 1 to 4 carbon atoms.

Preferred surfactants are those derived from polyethyleneoxy compound



wherein R is methyl and n is an average of from 5 to 20. Typical examples of the polyethyleneoxy compounds are methoxypolyethylene glycols of molecular weight 300, 400, 500 and 600.

The surfactant can of course be prepared separately and a small amount added to the prepolymer-forming mixture or to the formed prepolymer.

Formation of the prepolymers can be carried out by any of the known methods, i.e. by heating the components together or by allowing them to react at ambient temperature optionally in the presence of catalysts.

The emulsions of the prepolymers prepared by the methods described above are oil in water emulsions and may comprise from 99 parts to 10 parts by weight of water, from 1 part to 90 parts by weight of an organic isocyanate or prepolymer and a stabilising amount of a non-ionic surface active agent devoid of hydroxy, amino and carboxylic acid groups. It is preferred that the amount of water present be from 10—66% by weight of the isocyanate or prepolymer plus surface active agent. A preferred amount of the surface active agent is from 5 parts to 15 parts

by weight based on 100 parts by weight of isocyanate or prepolymer.

The emulsions can be prepared by conventional methods, either by mixing the emulsifying agent with the organic isocyanate or prepolymer and mixing this mixture with water or alternatively the non-ionic surface active agent can be prepared in situ in the isocyanate or prepolymer and this product, diluted if desired with further isocyanate, mixed with water and the whole agitated to obtain the desired emulsion.

The process of the invention is simply carried out by coating the pieces of scrap foam which may be in the form of small particles or even cutting dust with the oil in water emulsion and holding the mass of foam and emulsion under compression for a suitable period of time which may be easily determined by experiment. At ambient temperature several hours may be required to obtain a fully cured block of reconstituted foam but by using a heated press the time required can be reduced to a few minutes. Suitable compressions are from 2 times to 5 times by volume and temperatures of 70—100°C are suitable for a curing time of about 15 minutes.

The compression mould may be coated with a release agent or may be lined with a preferably water permeable facing such as paper, asbestos paper or cloth or any fibrous sheet. The facing and reconstituted foam will then be bonded together to give a block of surfaced foam.

The quantity of bonding agent i.e. isocyanate or prepolymer used may range from 10% by weight upwards based on the weight of foam scrap, about 10% being the least amount found necessary to achieve a satisfactory bond using optimum distribution by spraying the emulsion on to the agitated scrap; the upper level of usage will depend on the density required in the reconstituted material. The final density will in fact be a compromise between:

- (1) the amount of isocyanate or prepolymer used
- (2) degree of compression
- (3) density of the original foam scrap used
- (4) distribution of particle size in the foam scrap.

Amounts of from 10% to 70% by weight of bonding agent have been found convenient.

If increased density of reconstituted rigid foam scrap is desired, the scrap may be pre-compressed before bonding.

There may also be incorporated in the mixture of aqueous bonding agent and foam scrap, other particulate matter such as light weight varieties of concrete scrap, foundry sand, wood chip, cork, sawdust, expanded mica, fibrous materials and powdered fillers. Other scrap plastic materials such as scrap polystyrene may also be incorporated.

If desired silicates, silica sols and other nucleating agents and catalysts may also be incorporated.

In order to improve the fire resistance of reconstituted foam, water-soluble fire retardants, for example ammonium salts, urea, phosphates, borates, sodium hexametaphosphate and sodium pentaborate may be incorporated via the aqueous phase.

Reconstituted scrap polyurethane foam made by the above process is normally of higher density than unreconstituted foam and is suitable for flooring, for example in refrigerators and freezers in addition to being useful for thermal insulation generally.

The invention is illustrated by the following examples in which all parts and percentages are by weight except where otherwise stated.

#### Examples 1, 2 and 3.

A mixture of methylene bridged polyphenyl

polyisocyanates (100 parts) containing diisocyanate, triisocyanate and higher polyisocyanates made by phosgenation of an aniline/formaldehyde condensation product obtained by condensation in the presence of hydrochloric acid was reacted at 100°C for 30 minutes with a monomethylether of polyethylene glycol (average molecular weight 300) (5 parts). This mixture of polyisocyanates was emulsified with water in the proportions shown in Table I to give emulsions which were mixed with foam scrap in the amount shown. The mixture was then compressed to the degree shown in the table and held under compression for the times given in the table. In one case a catalyst "ARMEEN" DM116D was incorporated. (The word "ARMEEN" is a registered Trade Mark).

The reconstituted foam blocks were removed from the moulds and their physical properties were recorded in the table.

TABLE I

	Example 1	Example 2	Example 3
Rigid polyurethane foam scrap	100	100	100
Polyisocyanate + methoxy polyethylene glycol	60	30	27
Water	20	20	13
Armeen DM116D	—	—	0.07
Compression	5x	3x	2x
Compression time	1½ hours at 20°C	1 hour at 20°C	15 minutes at 80°C
Density mg/m <sup>3</sup>	90	75	60
Compression strength			
10%	88	55	87
25%	154	152	129
Modulus kN/m <sup>2</sup>	984	573	1025

#### Example 4.

100 parts of a mixture of methylene bridged polyphenyl polyisocyanate as in Example 1 was mixed with—

5 parts methoxy polyethylene glycol (MW 300)  
30 parts oxypropylated glycerol (MW 1000)

20 parts Tris(chloropropyl) phosphate (fire retardant)  
0.3 parts "ARMEEN" DM16D (tertiary amine catalyst)

The above mixture was allowed to react for 6 hours at room temperature to form prepolymer and surfactant simultaneously.

100 parts of the above product was emulsi-

fied with 50 parts water and 400 parts of scrap polyurethane foam coated with the emulsion whilst under agitation. The whole was then placed in a mould coated with paper and compressed to 3 times compression at 70°C.

After 15 minutes the reconstituted foam was removed from the mould and had set to a foam slab bonded to the paper.

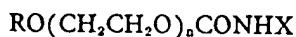
#### WHAT WE CLAIM IS:—

1. A process for bonding together polyurethane foam (as hereinbefore defined) scrap into a reconstituted block of foam which comprises coating the scrap with an aqueous oil in water emulsion of a mixture of methylene bridged polyphenyl polyisocyanates containing diisocyanates, triisocyanates, and higher functionality polyisocyanates or a prepolymer of such a mixture and holding the coated scrap in contact under compression until cured into a solid mass.

2. A process as claimed in claim 1 wherein the scrap is rigid polyurethane foam scrap.

3. A process as claimed in claim 1 wherein the aqueous oil in water emulsion contains a non-ionic surface active agent devoid of hydroxy, amino and carboxylic acid groups.

4. A process as claimed in claim 3 wherein the non-ionic surface active agent has the formula



wherein R is an alkyl group of from 1 to 4 carbon atoms, n is an integer such that the surface active agent contains an average of at least 5 oxyethylene groups and X is the residue

of a di- or poly-isocyanate and contains at least one free isocyanate group.

5. A process as claimed in claim 4 wherein the surface active agent contains an average of from 5 to 20 oxyethylene groups.

6. A process as claimed in either of claims 4 or 5 wherein R is methyl.

7. A process as claimed in any one of claims 3 to 6 wherein there is present from 5 to 15 parts by weight of surface active agent based on 100 parts by weight of isocyanate or, where a prepolymer is used in the process of the invention, on 100 parts by weight of prepolymer.

8. A process as claimed in any one of claims 3 to 7 wherein the amount of water present in the aqueous emulsion is from 10 to 66% by weight of isocyanate plus surface active agent or, where a prepolymer is used in the process of the invention, by weight of prepolymer plus surface active agent.

9. A process as claimed in claim 1 wherein the amount of isocyanate or prepolymer present in the aqueous emulsion applied is from 10% to 70% by weight of the foam scrap.

10. A process for bonding together polyurethane foam scrap into a reconstituted block of foam substantially as described herein with reference to any one of the Examples.

11. Blocks of reconstituted foam scrap whenever obtained by a process as claimed in any one of claims 1 to 10.

DONALD LEES,  
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.